"Harnessing Carrageenan-Encapsulated CuO and Ag Nanoparticles for Enhanced Drug Degradation and Sustainable Food Packaging"

SYNOPSIS

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Introduction

To ensure the long-term well-being of the natural world and human activities, a sustainable environment is one that is created and maintained during the course of human existence. It means protecting natural resources, cutting down on pollution and waste, and promoting ecological balance. Sustainable practices aim to satisfy present-day needs without compromising the ability of future generations to satisfy their own (Hazarika et al., 2022). These days nanotechnology has emerged as one of the most dynamic research areas. Nowadays, applications of nanotechnology can be found in material science, electrical engineering, chemistry, cosmetics, and sunscreens. To create nanoparticles, a variety of techniques are employed, including the chemical approach, hydrogel, sol-gel, co-precipitation, and green method. Except for the green method, all of these techniques rely on chemicals. Different plant parts, such as roots, leaves, bark, flowers, seeds, and stems, are employed in the green approach to synthesise nanoparticles. These plants are readily available and have therapeutic significance (Bhatia et al., 2022; Sharma et al., 2023).

The nanocomposites are synthesized by reducing the metal ions to the Nano range. Nanoparticles are used because of their high surface area to volume ratio which increases the chemical reactivity of nanoparticles. These days metal oxide or metal nanoparticles like ZnO (Chauhan et al., 2023), Ag and CuO nanoparticles (Bhatia et al., 2022) and many more are used for the synthesis of nanocomposite materials.

Plastic has been utilised as a packing material for the past few decades. Plastics are widely used because of their non-reactive nature, temperature resistance, excellent reliability, longevity, cost-effectiveness, and ease of use (Zhang et al., 2023). These days the plastic waste and drugs released in the environment are of measure concern. The plastic waste does not degrade completely and its accumulation in the environment leads to air, soil and water pollution. The drug released in the soil also leads to soil and water pollution (Hunge et al., 2023). By keeping in mind these two measure issues we try to find a green alternative of traditional plastic packaging and an effective

nanocomposite for drug degradation. Different nanoparticles or nanocomposites are employed in fields like, food industry, pharmaceuticals, cosmetics, drug delivery, paints etc. We have synthesized CuO and Ag nanoparticles and encapsulated them Carrageenan matrix for the synthesis of nanocomposites and nanocomposite films.

CuO nanoparticles

Copper (Cu) is used since ancient times to make utensils and also in medicines due to their antimicrobial properties. Copper is chemically less reactive, 100 % recyclable, resistant to corrosion and used in agriculture, wood preservation, anti-fouling paints, textile, wound healing etc. (Ramesh et al., 2023). Copper oxide is any material that contains both copper and oxygen. It can be further divided into two types: copper (I) oxide (Cu2O) and copper (II) oxide (CuO), each of which has distinct chemical properties and uses. Cu2O, or copper (I) oxide, is a reddish-brown chemical that can be synthesised. Copper oxide is a p-type semiconductor (Waris et al., 2021). It is an essential element in human nutrition. Copper oxide nanoparticles possess strong antimicrobial properties against bacteria, viruses, and fungi (Murugan et al., 2023). They disrupt cell membranes and generate reactive oxygen species (ROS), leading to microbial cell death. This makes them valuable in antimicrobial coatings, textiles, and water treatment.

Ag nanoparticles

Ag nanoparticles have a high surface area-to-volume ratio that facilitates better interaction with bacteria; silver nanoparticles have strong antimicrobial capabilities. They are helpful in wound dressings, water purification systems, and medical devices because they are efficient against a wide range of bacteria, viruses, and fungus. Silver nanoparticles are also utilised in biomedical applications, including medication administration, cancer therapy, and imaging, by virtue of their ability to be biocompatible and non-toxic at therapeutic doses (Zulfiqar et al., 2024). Silver nanoparticles exhibit catalytic activity, particularly in oxidation reactions. This property is utilized in catalysis for organic transformations, pollutant degradation, and fuel cell applications. Silver nanoparticles are highly conductive, making them essential in electronic applications such as

conductive inks, sensors (Zhan et al., 2023), and transparent conductive coatings for displays and solar cells.

Argemone maxicana and *Argemone albiflora*

We have used two different species of *Argemone* plant for the synthesis of CuO and Ag nanoparticles. *Argemone maxicana* commonly known as Mexican prickly poppy (Patocka et al., 2024) and *Argemone albiflora* commonly known as bluestem prickly poppy, leaf extract were used in amalgamation of copper oxide and silver nanoparticles respectively. This plant has been traditionally used since ancient times for treating jaundice, chest pain, asthma, liver ailments, and as a remedy for blood disorders (Yuan et al., 2023). *Argemone* is a wide herb commonly found in arid regions all over India. This plant is medicinally important and used for the treatment of different infectious diseases from ancient times. We have used Argemone because this plant is not edible and not consumed by the animals due to the fine spine present on the plant.

Carrageenan

Carrageenan, derived from seaweed, is biocompatible and non-toxic, making it suitable for biomedical and pharmaceutical applications. When used as a coating or encapsulating material for nanoparticles, carrageenan ensures that the encapsulated payload remains safe and does not cause adverse reactions in biological systems (Zakaria et al., 2023). Its biodegradability and renewable sourcing contribute to sustainability efforts in nanoparticle-based technologies. Carrageenan is generally recognized as safe (GRAS) by regulatory agencies like the FDA for food and pharmaceutical applications, which facilitates the regulatory approval process for products incorporating carrageenan-encapsulated nanoparticles. Carrageenan, a natural polysaccharide derived from red seaweed, can act as a stabilizing agent for nanoparticles. The nanoparticles, Ag and CuO in this case, are encapsulated within the carrageenan matrix through solution casting method in a single step.

Literature review

The goal of the current study was to create copper oxide nanoparticles (CuONPs) by employing an aqueous extract of *Mangifera indica* as a biologically generated reducing agent. Under visible light, the synthesised CuONPs were used as a photo-catalyst to degrade malachite green. With a high degrading efficiency of 95.39%, the CuONP's exceptional performance was facilitated by its outstanding band gap energy of 1.62 eV. Over the course of five recycling cycles, the CuONPs likewise showed excellent endurance. Furthermore, under light circumstances, the CuONPs had shown considerable antibacterial activity against strains of S. aureus and E. coli, surpassing their activity in the absence of light (Dat et al., 2023).

According to this study, the main goal was to create copper oxide nanoparticles (CuONPs) utilising Canthium coromandelicum leaves in an easy, affordable, and sustainable way. According to the photocatalytic evaluation, the synthesised CC-CuONPs showed an impressive 91.32% degradation efficiency for methylene blue (MB) and 89.35% degradation efficiency for methyl orange (MO). These findings imply that the biosynthesised CC-CuONPs may be able to remove pollutants from the environment in an efficient and sustainable way (Selvam et al., 2022).

In the current work, an aqueous extract of Calotropis procera was used to create copper oxide nanoparticles (CuO NPs). XRD examination revealed that the nanoparticles had a highly crystalline structure and ranged in size from 40 to 100 nm. The spherical shape of the 20–80 nm-sized nanoparticles was verified by SEM and TEM pictures. The produced CuO NPs' anti-bacterial and anti-fungal properties were assessed. In vitro and detached leaf assays of Muskmelon, both phytopathogens showed substantial suppression at a dose of 100 µg/mL (Shah et al., 2022).

The potential of green synthesised AgNPs, which can be employed as antibacterial, antifungal, antiviral, and anticancer medicines, is thoroughly discussed in this paper. Following a brief introduction, we talked about the most recent research on the synthesis of AgNPs from various plant extracts, such as those from leaves, seeds, flowers, stems, bark, roots, and entire

plants. The varied therapeutic activities of AgNPs against different bacteria, fungi, viruses, and malignancies, such as lung, prostate, and breast cancers, were highlighted in the section that followed. Next, we emphasised AgNPs' overall mode of action. The paper went on to describe the benefits of the green synthesis method over chemical and physical approaches (Arshad et al., 2023).

Much research has been done on the use of green synthesised nanoparticles (NSPs) in food packaging. Filler is necessary for biopolymers to improve the mechanical, optical, barrier, thermal, and antibacterial qualities of packaging. Green synthesised NPs added to biopolymer packaging should improve performance and lessen environmental harm at the same time. The current review paper focuses on biopolymer films that contain bio (green) synthesised nanomaterials and how well they work to lessen the harmful effects that synthetic packaging has on the environment. It also addresses the potential, functionality, and most recent advancements of bio-nanocomposite films and coatings in biodegradable food packaging. It also covers the broad principles of green synthesis of NPs, their production processes, performance, and characterisation (Jafarzadeh et al., 2023).

In the present work, based on chitosan (CS), nanosized TiO2, and black plum peel extract (BPPE), multifunctional food packaging sheets were created. We looked into how BPPE and/or TiO2 affected the functional and physical characteristics of CS film. Nine phenolic compounds containing 23.29% anthocyanins were found in BPPE, according to results. If TiO2 and/or BPPE are added, the physical characteristics of CS film may change substantially. In particular, CSeTiO2, CS-BPPE, and CSeTiO2-BPPE films all had superior mechanical strength and greater barrier qualities than CS film against water vapour and UV–vis radiation. Both CS-BPPE and CSeTiO2-BPPE films had significant free radical scavenging capacity, according to an antioxidant experiment (Zhang et al., 2019).

In this work, a one-step hydrothermal approach was effectively used to synthesise copper sulphide nanoparticles (CuS NPs) with a photothermal effect, which were then uniformly dispersed in natural carrageenan (Carr)

to generate Carr/CuS films, which help prevent food spoiling due to microbial contamination. The broad-spectrum antibacterial activity of the Carr/CuS film against Staphylococcus aureus (99.9%) and Escherichia coli (99.2%) was verified by photothermal-induced antibacterial tests. A beef antibacterial test also demonstrated that near-infrared (NIR) irradiation greatly enhanced the Carr/CuS film's antibacterial activity against germs on the food sample. Furthermore, the high-transparency Carr/CuS film demonstrated improved mechanical and thermal stability as compared to the Carr film (Li et al., 2020).

In this work, using a hydrothermal technique, titanium dioxide nanotubes (TNTs) and CuO-doped TNTs (TNT−CuO) were synthesised and added to films based on carrageenan. The development of homogenous nanocomposite films was confirmed by the SEM data. The carrageenan film gained mechanical strength, surface hydrophobicity, and water vapour barrier qualities when nanoparticles were added. It also acquired UV-blocking capabilities. Under visible light, the carrageenan films containing modified TiO2 (TNT and TNT−CuO) exhibited notably greater antibacterial activity compared to the TiO2-added film. After 12 days of storage at 20 °C, bananas packaged with the neat carrageenan and TiO2-added films significantly deteriorated (Ezati et al., 2021).

The goal of the current work was to create antimicrobial films based on carbohydrate biopolymers for use in food packaging. Solvent casting was used to create the nanocomposite films containing different biopolymers and copper oxide nanoparticles (CuONPs). The composite films' antibacterial activity, water vapour permeability, UV protection, and thermal stability were also assessed. The nature of the polymers employed determined the surface morphology of the films. The CuONPs' crystallinity in the composite films was shown by XRD. The thickness, tensile strength, water vapour barrier property, relative humidity, and UV barrier property were all raised with the addition of CuONPs. Strong antibacterial action was shown by the CuONPs integrated composite films against Listeria monocytogenes and Escherichia coli. The created composite films might be

applied as active UV-light-blocking antibacterial packing films (Shankar et al., 2017).

In this work by using κ-carrageenan, silver nanoparticles (AgNPs), and an organically modified clay mineral (Cloisite® 30B), antimicrobial bionanocomposite films were created. AgNP-containing nanocomposite films demonstrated strong UV barrier qualities as well as the AgNPs' distinctive plasmonic effect, with the highest absorption occurring at 420 nm. Tensile strength (TS) and water vapour permeability (WVP) of the nanocomposite films rose and decreased by 12–27% and 14%, respectively, in comparison to the neat carrageenan film, depending on the type of nanofillers used. The harmful bacteria, including Gram-positive (Listeria monocytogenes) and Gram-negative (Escherichia coli O157:H7), were susceptible to the antibacterial activity of the nanocomposite films. The nanocomposite films containing AgNP exhibited potent antibacterial activity against Gram-negative bacteria, whereas the films containing clay demonstrated potent antimicrobial activity against Gram-positive bacteria (Rhim et al., 2014).

In this work ZnO/α-Fe2O3 nanosheets were created using hydrothermal and total reflux techniques. A hexagonal structure and nano-sized crystallites with a mean size of roughly 35 nm were revealed by XRD pattern analysis. Under UV–vis irradiation, the photo-degradation of the medication cefixime trihydrate in an aqueous solution was studied to determine the photocatalytic activity. The optimal values for ZnO/α-Fe2O3 concentration, cefixime trihydrate concentration, UV–vis light intensity, and irradiation time were found to be 0.41 g·L−1, 10.11 mg·L−1, 8 W·m−2, and 127 min, respectively. Under the optimised circumstances, the highest degrading efficiency was attained at 99.1% (Shooshtari et al., 2017).

In this work, AgBr was in situ interspersed on CeO2 to create CeO2-Ag/AgBr composite photocatalysts with a Z-scheme arrangement, which were then photoreduced. When exposed to visible light, the CeO2-Ag/AgBr composites showed increased photocatalytic activity for the

photodegradation of ciprofloxacin (CIP). In-depth research was done on the impacts of different inorganic salts and the initial CIP concentration. Excitation–emission matrix fluorescence spectra in three dimensions were employed to track the breakdown of the CIP molecule in more detail. Based on LC-MS equipment, plausible degradation mechanisms for CIP were suggested (Wen et al., 2018).

In the current study, a bifunctional catalyst with oxygen vacancy, magnetic γ-Fe2O3–MnO2, was synthesised for the activation of peroxymonosulfate (PMS) under visible light. By using ciprofloxacin (cipro) degradation, the activity of γ-Fe2O3–MnO2 was examined. The findings shown that in a visible-light/PMS system, 98.3% of the cipro (50 μM) was eliminated in 30 minutes thanks to γ-Fe2O3–MnO2 (2:1) with precisely adjusted oxygen vacancy. The pseudo-first-order kinetic model, with the greatest kinetic constant of 0.114 min−1, fit the cipro degradation data quite well. In addition, the γ-Fe2O3–MnO2 demonstrated practicability, stability, and recycling. In the visible-light/γ-Fe2O3–MnO2/PMS system, a high selectivity for cipro degradation was found with coexisting anions (Zhao et al., 2021).

The purpose of present work is pollutant degradation in the presence of visible light, copper (Cu) and silver (Ag) nanoparticles and their nanocomposites at different ratios were investigated. The model pollutant utilised to compare the catalytic activity of the nanomaterials was para-nitrophenol (p-NP). The most active photocatalyst was discovered to be the silver rich nanocomposite (CuAg2) because to its enhanced light harvesting capabilities and the cooperative charge transfer between Ag and Cu. In the presence of a modest quantity of H2O2, CuAg2 might photocatalytically mineralize drugs like norfloxacin (NOR) and sulfamethoxazole (SMX). The breakdown of the contaminants was discovered to be caused by photogenerated hydroxyl radicals (Pramanick et al., 2023).

In this work a very simple and economical approach was used to manufacture the carbon nano-onions (CNOs), polyanilin nanotubes (PANI-NTs), and gold nanoparticles (AuNPs) composites. To do this, the

synthesised nanocomposite was first examined using techniques such as transmission electron microscopy, scanning electron microscopy, and X-ray diffraction spectrometer. Subsequently, the CNOs/PANI-NTs/AuNPs nanocomposite was added to a glassy carbon electrode (GCE) and utilised to evaluate CIP in an aqueous media. The results indicated that the developed sensor has a very good ability to measure in real samples, with the detection limit for this drug in the concentration range of 5 nM to 80 μM equal to 1.3 nM. Additionally, in the presence of visible light, the produced nanocomposite can destroy this medication by up to 99% (Teymourinia et al., 2023).

Research gap identification

There is limited literature available on the synthesis of Copper oxide (CuO) and Silver (Ag) nanoparticles using *Argemone* plant extract and their encapsulation with Carrageenan in one step. This study aims to investigate and enhance the properties of CuO, Ag nanoparticles and their respective nanocomposites/nanocomposite films synthesized through a green approach. Furthermore, the synthesized nanostructures will be explored for their potential photocatalytic and packing applications.

Objectives

Based on the aforementioned discussion, the current study aims to achieve the following objectives:

- To investigate the synthesis of copper oxide and Silver nanostructures using a solution casting method, by utilizing an extract of *Argemone maxicana* and *Argemone Albiflora* leaves for the green synthesis process.
- To investigate the synthesis of Carrageenan encapsulated CuO and Ag nanocomposites/nanocomposite food packaging films.
- To characterize by using various techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM).
- To study the photocatalytic applications of synthesized CuO and Ag based nanocomposites.

- To study the food packaging application of nanocomposite food packaging films.

Proposed methodology

Materials

Copper sulphate ($CuSO_4$), Silver nitrate ($AgNO_3$), Sodium hydroxide (NaOH) and Carrageenan purchased from Merk Chemicals. For plant extract preparation, leaves of *Argemone maxicana* and *Argemone albiflora* collected from nearby river banks.

Leaf extract preparation

Argemone maxicana and *Argemone albiflora* leaves were freshly harvested and well-cleaned from a nearby riverbank. The leaves were divided into smaller bits after being dried at room temperature. For 30 min at 100°C, 4 g of freshly chopped Argemone albiflora leaves were boiled in 100 mL of double-distilled water (Tellez-de-Jesus et al., 2021). The plant extract was utilised to create copper nanoparticles after cooling to room temperature and filtering via Whatman filter paper.

Synthesis of nanocomposites and nanocomposite films

Bio- nanocomposite and nanocomposite films were synthesized in single step by following solution casting technique with some modifications (Zhang & Jiang., 2020). $0.1mM$ solution of $CuSO_4$ and $AgNO_3$ was prepared and permitted constant mixing at 70°C on a magnetic stirrer. Plant extracts of different concentrations 30, 60 and 90 mL were added to the above solutions dropwise. Once reduction process is completed Carrageenan was added and stirred for 20 min. the above solution is then cooled and filtered to obtain nanocomposites.

For the synthesis of nanocomposite films, we have added Carrageenan and glycerol to the reduced solution and poured this mixture in petriplates and allow to dry at room temperature for 2 days.

Characterization of synthesized nanocomposite

A wide range of methods were used to carefully examine the properties of the fabricated nanostructures. The angle of diffraction within a given range was measured using X-ray diffraction (XRD). An energy dispersive analysis-equipped high-resolution scanning electron microscope (SEM) was used to assess the surface morphology. High-resolution transmission electron microscopy (TEM) was used to evaluate the sample's size and form. The sample's absorbance was measured using UV-visible spectroscopy and the mineral composition and physical characteristics were examined using Fourier transform infrared spectroscopy (FTIR). The mechanical properties of the nanocomposite films were examined by Universal Testing machine.

Thesis Outline

The thesis will be comprised of following chapters:

Chapter 1 (Introduction): This chapter gives a brief introduction to nanotechnology, stressing the properties of CuO and Ag nanoparticles, carrageenan and respective nanocomposites and the potential of plant extract from *Argemone maxicana* and *A. albiflora*. It further defines the goals of the proposed research.

Chapter 2 (Literature Review): This section will focus on a comprehensive exploration of profound literature concerning the synthesis, characterization, and usage of nanocomposites made of carrageenan and CuO and Ag nanoparticles. Additionally, it will address the identification of gaps in existing research.

Chapter 3 (Materials and Methods): This section will provide a comprehensive discussion on the properties of and CuO nanostructures, including their composition, environmentally friendly production techniques, characterization methodologies, and various applications.

Chapter 4 (Results ad Discussion): This section will present the analysis of the findings from the research conducted on the physical and chemical characteristics of nanostructures of NiO and CuO. The chapter will contain detailed reports on the properties observed, followed by an in-depth analysis and

interpretation of the results.

Chapter 5 (Summary and Conclusion): In conclusion, this chapter provides a comprehensive summary of the entire study, highlighting its relevance to the stated objectives.

Chapter 6 (References): In this section, the cited sources will adhere strictly to the Harvard referencing style.

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CERTIFICATE
(SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the Synopsis/Revised Synopsis for Ph.D. Thesis titled, **"Harnessing Carrageenan-encapsulated CuO and Ag nanoparticles for Enhanced Drug Degradation and Sustainable Food Packaging"**, submitted by **Ms. Shilpa Kumari** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the Division/Department of **Chemistry**, School of **Basic and Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 20-06-2024.

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